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(54) Catalyst regeneration method and apparatus

(57) A method and apparatus are disclosed which permit one or a plurality of different chemical reaction processes e.g. hydrocarbon reforming and desulphurising, wherein different catalytic species are employed to utilize common regeneration facilities. This result is achieved by operating a catalytic regenerator system in a blocked fashion wherein each different catalytic species is alternately regenerated. In one particular embodiment, two catalysts of different chemical composition are alternately regenerated using a common regeneration facility. In another embodiment, two different catalytic species having the same original composition, but differing in degree of deactivation are alternately regenerated using a common regeneration facility.

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Fig. 1.

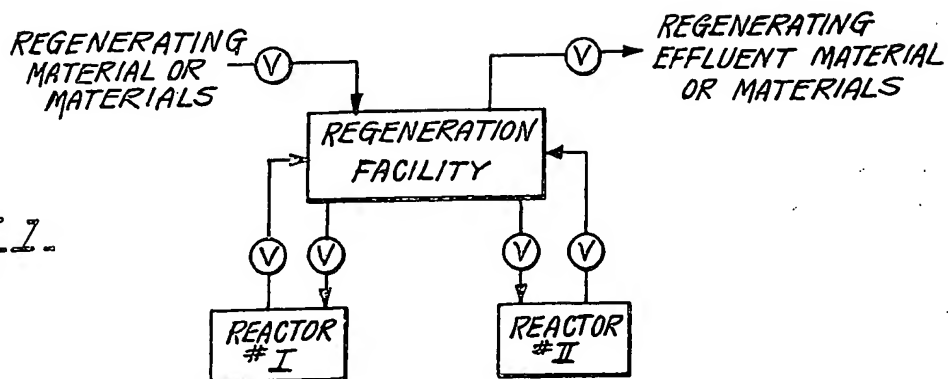


Fig. 2.

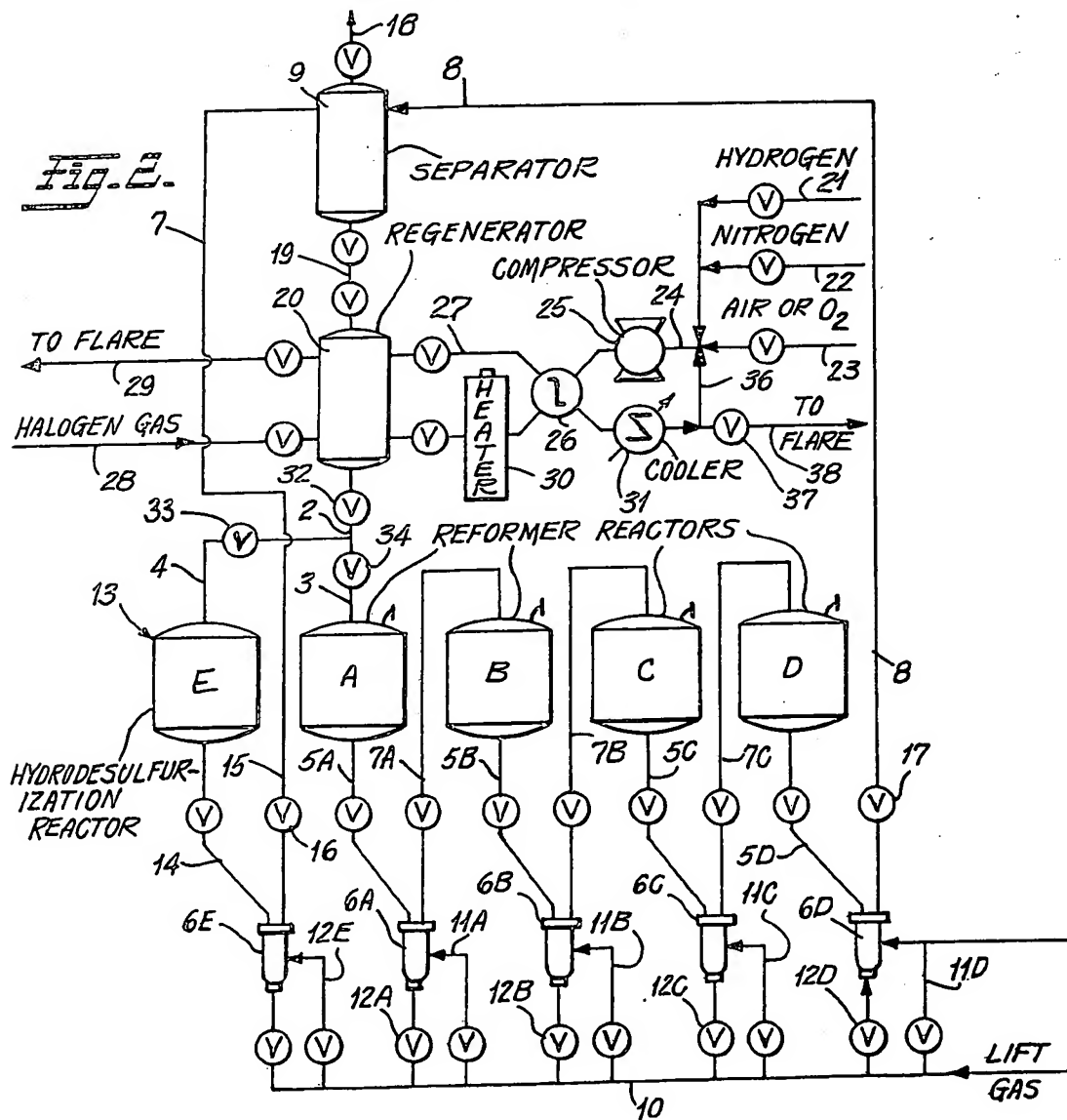


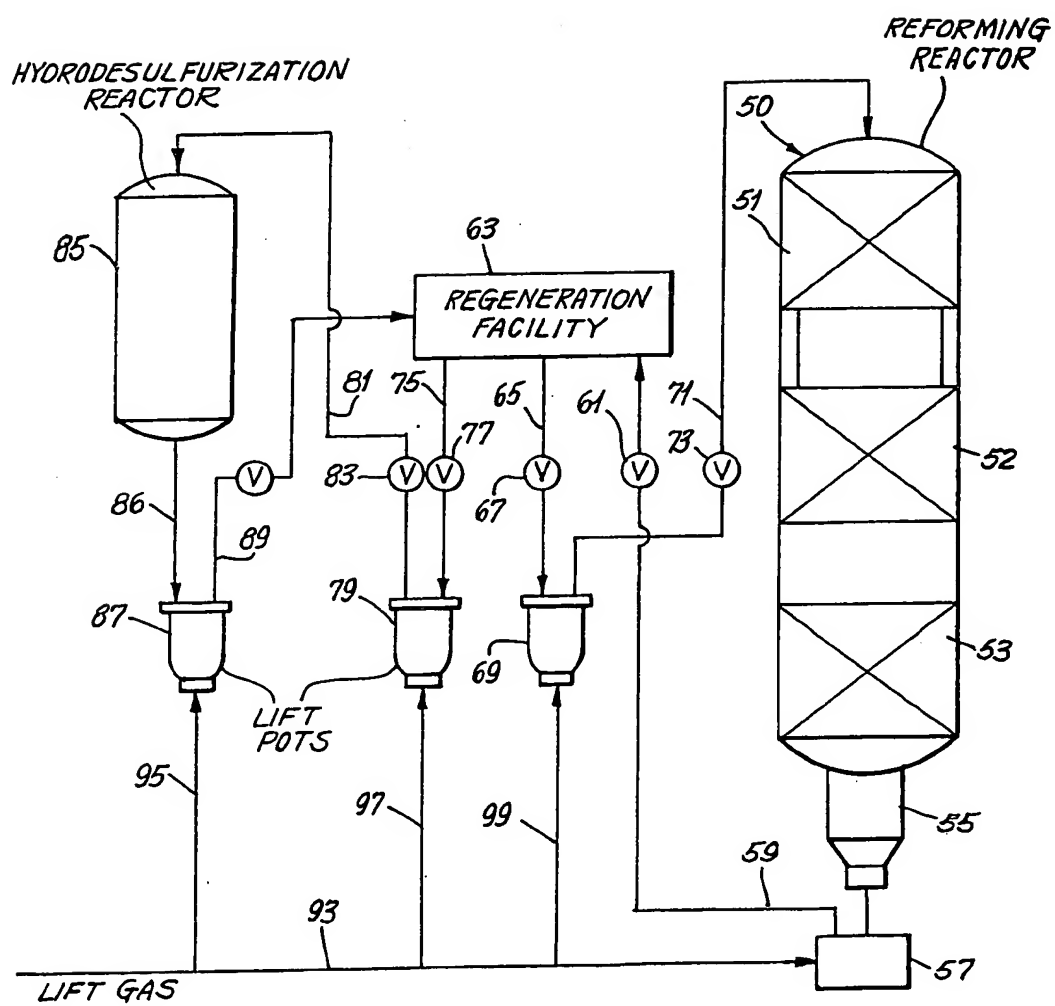
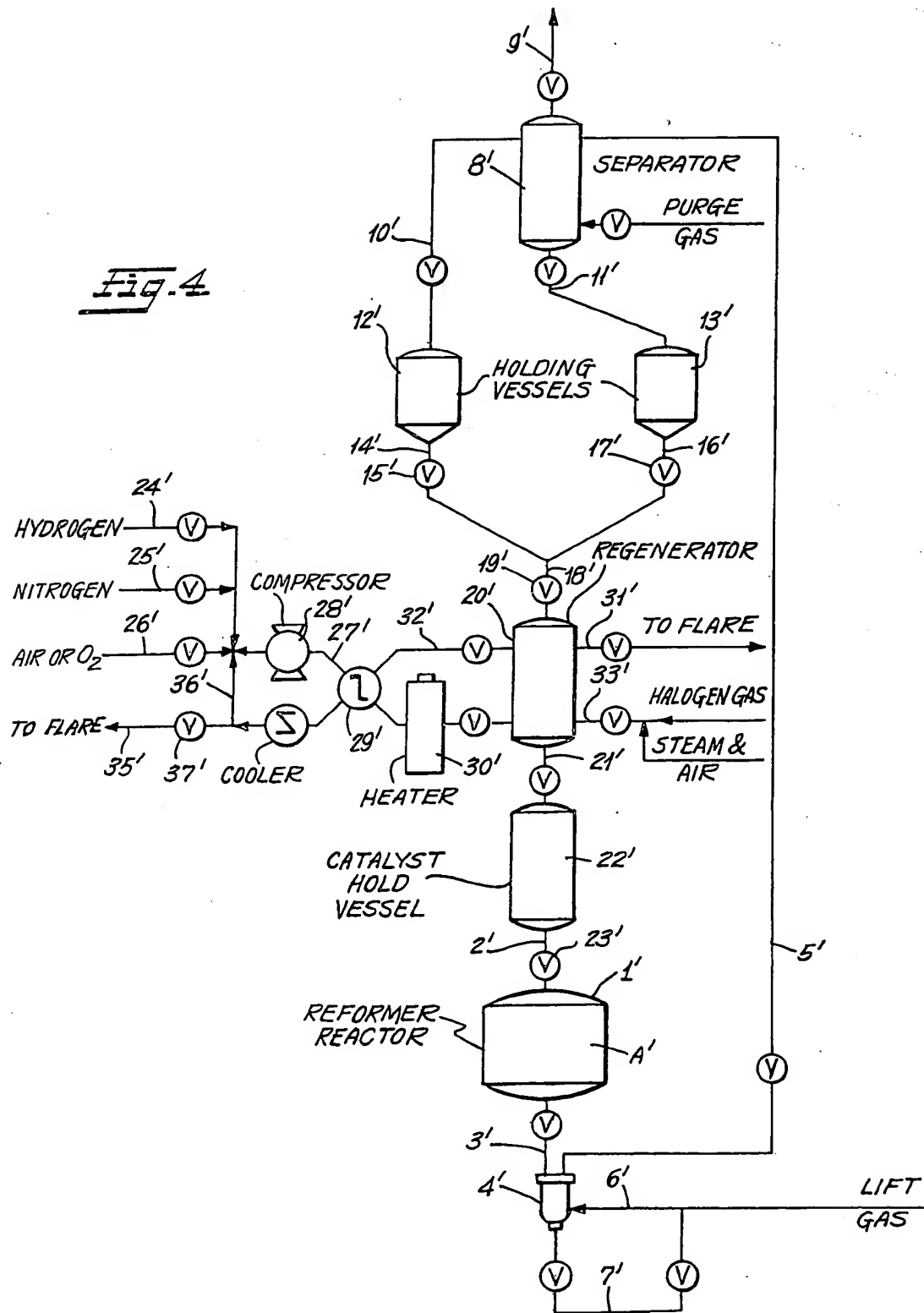
Fig. 3.

Fig. 4

SPECIFICATION

Catalyst regeneration method and apparatus

5 The present invention relates to a method and apparatus for the regeneration of catalysts employed in chemical processing. It is particularly concerned with the regeneration of different catalysts employed in two or more organic or inorganic chemical reaction treatment processes using a common regeneration facility.

The present invention is applicable to any refining, petrochemical, or other chemical treatment process wherein different catalysts are employed. The present invention is equally useful for the regeneration of the same type of catalyst which is used in different reaction processes. It may also be advantageously employed for the regeneration of different catalysts used in different chemical processes. Examples of such chemical processes are catalytic cracking, isomerization, hydrogenation, dehydrogenation, reforming, hydroforming, aromatization, alkylation, polymerization, hydrosulfurization, and oligomerization. The present invention may be also utilized for the regeneration of catalysts employed in the processing of the same or different feeds. It is additionally useful for the regeneration of the same type catalyst where it is employed in processing different types of feed requiring two entirely different operating conditions. In short, the present invention is advantageous wherever it is desirable to separately regenerate two populations of catalyst.

The present invention may also be used for the separate regeneration of liquid catalysts, or solid catalysts. It is particularly useful in the regeneration of the catalysts used in the hydrosulfurization and reforming of naphtha fractions. These latter two processes may be carried out either separately or in combination.

The reforming of hydrocarbons such as a naphtha fraction by utilizing a platinum group metal-containing catalyst, such as platinum with or without other promoters, is well known to those trained in the art. In these reforming operations, the naphtha feedstock is admixed with hydrogen and contacted, in a gaseous physical state, with a platinum group metal-containing catalyst under reforming conditions of elevated temperature and pressure to cause at least a portion of the feedstock to be converted to more valuable products such as higher octane motor gasoline, gasoline boiling range materials and also the separable materials contained therein such as benzene, toluene, and xylenes.

However, it is well known to those skilled in the art that the naphtha feedstock to be reformed must be relatively free of impurities such as sulfur and heavy metals to take advantage of the present technology. Accordingly, it is the practice in the more recent reforming art to subject the naphtha fraction to a feed hydrotreatment (often referred to in a less definitive manner as a hydrosulfurization process) prior to reforming. Conventionally, a hydrosulfurization process is employed in which the naphtha fraction is catalytically treated with hydrogen to con-

vert the sulfurous impurities, such as mercaptans, disulfides, porphyrins, and their derivatives, to hydrogen sulfide which is subsequently stripped from the naphtha by means well known to those trained in the art prior to use as a reformer feed.

Most solid catalysts employed in chemical reaction processes, though, are subject to deactivation as a result of the deposition of hydrocarbonaceous material (often referred to as "coke") on the catalytic surface. The hydrocarbonaceous coke is deposited in the catalyst pores and on the surface of the catalyst particles. This material coagulates and polymerizes on the catalytic surface, thereby leading to the formation of coke deposits both inside and outside the catalyst particles which render the catalytic surface inaccessible to fresh reactants. As this deposition on the catalyst continues, the catalytic activity decreases until either fresh catalysts must be substituted for the deactivated catalyst, or the deactivated catalyst must be regenerated. In hydrosulfurization reactions, the metal compounds contained in the feed, such as arsenic, have an added permanent deleterious effect on the life of the catalyst.

It is evident, therefore, that most catalytic petroleum treatment processes require the regeneration or replacement of the catalyst at periodic intervals. Since these catalysts frequently contain precious metals, it is desirable to regenerate or reuse the catalyst as much as possible since the recovery of the precious metals in spent catalysts and subsequent impregnation on a new support is a time-consuming and expensive procedure. Accordingly, the prior art has developed many processes and apparatus for the regeneration of catalyst particles. These processes can generally be characterized as falling within two types, those that occur in an external regeneration apparatus and those that occur *in situ* within a process reactor. The instant invention particularly relates to those regeneration processes which occur in an external regeneration apparatus.

Separate regeneration facilities are required in those catalytic processes among others which employ a fluidized catalyst or a moving bed catalyst system. In the fluidized catalyst system, the process reactor is charged with a finely divided catalyst of particle size in the range 1 to 200 microns. The catalyst particles are then contacted with a hydrocarbon charge and may also be in admixture with a gas stream such as hydrogen gas which serves to fluidize the catalyst particles.

In a moving bed system, the catalyst particles move in a gravitational flow through a reactor. Catalyst is withdrawn from the bottom of the reactor to maintain the desired catalyst activity as fresh or freshly regenerated catalyst enters the reactor top. The spent catalyst is then regenerated in an external facility and returned to the reactor.

Heretofore, however, those processes employing an external regeneration facility have required a separate regeneration facility for each separate process. The prior art has not developed a method whereby common regeneration facilities could be utilized by two or more different processes wherein different catalyst species are employed. For exam-

ple, U.S. Patent No. 2,901,421 discloses a typical prior art regeneration system in which each process reactor requires its own catalytic regeneration unit. Likewise, U.S. Patent No. 3,011,968 teaches only a

5 system for the *in situ* regeneration of several reactors of the same process. Each process of the fluidized catalyst or moving bed catalyst type still requires its own separate regeneration facility. Similarly, U.S. Patent No. 2,902,435 discloses only the
10 separate regeneration of two separate components of a catalytic mechanical mixture used conjointly in the same reforming process. Each separate component of the mixture requires its own regeneration facility for reactivation.

15 One significant factor in the failure of the prior art to develop a regeneration system which can be conjointly utilized by two or more catalytic species is the fact that different process steps frequently require chemically different catalysts. For example, the
20 catalyst employed in reforming operations typically comprises a platinum group metal, preferably platinum, one or more of another metal such as germanium, iridium, tin, or rhenium, and a halogen group such as chloride on a suitable refractory inorganic oxide support, preferably alumina. In contrast,
25 a hydrodesulfurization catalyst typically comprises molybdenum and/or cobalt and/or nickel and/or compounds thereof on a highly porous support such as alumina. Since each of these different catalysts
30 often requires different regeneration conditions in order to maintain the optimum activity of the catalyst, the prior art has not previously developed a regeneration system which permits two or more
35 processes employing different catalyst species to utilize common regeneration facilities. Moreover, the prior art has not yet developed a regeneration system which would allow a single process which employs a two or more component catalyst, such as
40 described in U.S. Patent No. 2,902,435, to utilize a single regeneration facility for the reactivation of each catalytic component, where these components must be regenerated independently of each other.

It would be desirable, therefore to employ a single regeneration facility for two or more processes
45 wherein different catalysts are employed which must be regenerated independently of each other. It would also be desirable to utilize a single regeneration facility for the reactivation of a single process catalyst which comprises two or more components
50 which must be regenerated independently of each other.

Accordingly, the present invention provides, in one aspect, a method which permits two or more different catalytic materials employed in at least one
55 chemical reaction process to utilize common regeneration apparatus, the method comprising operating the regeneration apparatus in alternating regeneration cycles, each different catalytic species desired to be regenerated having its own regeneration cycle
60 associated therewith, and each of the regeneration cycles comprising:

a) transporting a stream of one of the catalytic species which has suffered a decrease in activity by exposure to chemical reaction conditions to the
65 regeneration apparatus;

b) treating the catalytic species therein to adjust its activity to desirable levels; and

c) returning the treated catalytic species to its respective chemical reaction process.

70 The present invention thus provides a method and apparatus for the regeneration of chemically and/or physically different catalysts, for example, petrochemical process catalysts. The catalysts are regenerated in a common regeneration facility. In
75 accordance with the present method it is possible to utilize a common regeneration facility to regenerate two or more catalytic species which have the same chemical composition, but differ in degree and/or type or deactivation.

80 It is also possible to use the present method for the reactivation of each of two or more components of a process catalyst, where each component must be regenerated independently of each other, and to use a common regeneration facility for the reactivation
85 of each component; or for the reactivation of two different petrochemical process catalysts, such as a hydrodesulfurization catalyst and a naphtha reforming catalyst.

The method of the present invention is equally
90 advantageous in the regeneration of catalytic materials which must be independently regenerated of each other, employed in either different or the same chemical processes. In one particular embodiment, the present invention enables a hydrodesulfurization
95 process and a catalytic reforming process to utilize a common regeneration facility. By operating a regenerator system in a blocked fashion, a single regenerator is able to maintain two different catalyst inventories at their optimum activity.

100 According to a further aspect of the present invention, there is provided an apparatus for the regeneration of at least two catalytically active species, employed in at least one chemical treatment process, requiring different regeneration procedures which
105 apparatus comprises a regenerator; a means for supplying a regeneration agent to the regenerator; a means for alternately supplying a stream of each of said catalytic species to the regenerator for treatment therein; and a means for returning the regenerated catalytic species to its petroleum treatment process. In the preferred embodiment, the regenerator
110 comprises a carbon burn-off zone or step, a halogenation zone or step, and a drying zone or step. A pneumatic transfer lift apparatus is used to transfer the deactivated catalytic material to the regenerator.
115 Preferably, the means for supplying the regeneration agent to the regenerator comprises a compressor to circulate the agent; a heat exchanger for transferring heat from an effluent stream of regeneration agent
120 to a fresh stream of regeneration agent; a heater to control the temperature of the regeneration agent entering the regenerator; and a cooler for cooling an effluent regeneration agent before it is vented to the atmosphere.

125 Preferred embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a block diagram illustrating the inventive concepts of the present invention;

130 Figure 2 illustrates a flow scheme according to one

embodiment of the present invention in which two chemically distinct catalysts employed in two different processes commonly utilize a regeneration facility;

5 *Figure 3* is a flow scheme similar to *Figure 2* in which a single reactor containing a plurality of treatment zones is substituted for the multiple reactor system shown in *Figure 2*; and

Figure 4 is a flow scheme according to a second embodiment of the present invention in which two separate catalytic components employed in the same process utilize the same apparatus for regeneration.

Referring to the drawings, *Figure 1* is a block flow diagram illustrating the application of the instant invention for the regeneration of any two catalytic species contained in any two different reactors. Each of the reactors I or II may process the same feed or different feeds. They may be performing identical chemical treatments or different treatments. The catalysts contained therein may be in any physical states, i.e. gaseous, liquid or solid. The two catalytic species may have different chemical compositions or they may have the same composition but differ in the degree or type of deactivation. Each of the catalyst species is alternately transported to the regeneration facility and treated therein by exposure to a regenerating material or materials to restore its activity to desirable levels.

30 The regeneration facility may be of any structure suitable for the particular treatment desired. It may be operated continuously or even cyclically. The regeneration materials may be any suitable agents required to restore the activity of the particular catalyst species enjoying the benefits of the instant invention, and may restore the catalyst activity by removing a deactivating material, adding an activating material thereto, or by drying the catalyst species. For example, the regeneration material may be gases, liquids, or even solids, such as an oxygen containing gas, a water containing gas, solid adsorbants, ion exchange particles, etc. In short, the instant invention enables any two catalytic species which require independent regeneration to utilize the same regeneration facility simply by operating the regenerator in an alternating series of regeneration cycles, each of the catalyst species having its own regeneration cycle associated therewith. In between each regeneration cycle, it may also be desirable to purge the regenerator to prevent contamination of the incoming catalyst species. Suitably, this purging can be achieved by employing an inert gas, which may contain oxygen, to remove any contaminants from the system.

55 *Figure 2* illustrates one embodiment of the instant invention in which two different petroleum treatment processes share a common regeneration apparatus. For ease of description, the present invention will be described with reference to the combination of a naphtha hydrosulfurization process and a naphtha reforming process, although it is clear that the instant invention is applicable to any combination of petrochemical or other treatment processes wherein catalysts are employed which must be regenerated independently of each other.

By way of description, but not limitation, other processes which may commonly utilize a regeneration facility according to the present invention include catalytic cracking, isomerization, hydrogenation, dehydrogenation, aromatization, alkylation, cyclizing, and desulfurization processes. The instant invention is particularly applicable to those systems of the gravitating bed type, although it is equally useful in those processes employing a fluidized bed.

10 Referring to *Figure 2*, in which for simplicity only the piping for the transport of solid catalyst is shown, a typical naphtha reforming system comprising reactors A, B, C and D is illustrated. Any reforming system well known to those skilled in the art may benefit from the advantages of the instant invention, including systems utilizing a single reactor vessel, or multiple reactor systems. The only requirement for the particular system chosen is that it requires an external regeneration facility. Generally, those systems utilizing a reactor of the gravitating or fluidized bed type require an external regeneration facility. *Figure 2* illustrates the application of the instant invention to a naphtha reforming system comprising four reactor vessels A, B, C and D of the gravitating bed type, although the instant invention is not limited in application to only such a system. It will be obvious to one skilled in the art, that, with minor modifications, a fluidized bed system could also be employed. The reactor vessels themselves may be of any design well known to the art, and may internally incorporate features for accomplishing uniform flow, contacting, and disengaging of the catalyst and reactant.

Reforming catalyst enters reactor vessel A through catalyst feed conduit 3 and control apparatus 32 and block valve 34 whereupon it contacts a naphtha charge as it descends through the vessel A. A stream of recycle hydrogen gas in admixture with naphtha charge, not shown, is also fed into reactor A which functions both as a heat sink and to suppress the formation of carbonaceous deposits on the catalyst surface as the reforming reactions proceed. The reactants proceed in this typical reformer process scheme from reactor A, through a heater to reactor B and so on to reactors C and D under conditions which are well known to those skilled in the art. Representative of a typical system for feeding a naphtha charge into and through a four reactor reforming system is U.S. Patent No. 3,011,968, herein incorporated by reference.

50 The particular reforming catalyst employed may be any of those well known to the art. By way of illustration, but not of limitation, typical examples include platinum-germanium-halogen on alumina catalysts, platinum-halogen on alumina catalysts, platinum-halogen-rhenium on alumina catalysts, and platinum-halogen-iridium on alumina catalysts or combinations thereof. Any method well known to the art can be used to prepare these catalysts. One particular method for the preparation of the platinum-halogen-rhenium catalysts is described in U.S. Patent No. 3,496,096.

After passage through reactor A, the catalyst descends through gravity feed leg 5A into lift pot 6A. Lift pot 6 may be of any design familiar to those

skilled in the art. One suitable example is the lift pot disclosed in U.S. Patent No. 2,901,421. The solid granular catalyst stream is then transferred by pneumatic lift pipe 7A to reactor B. It should be obvious of course, that a mechanical transfer apparatus may also be employed. The granular catalyst descends similarly through reactor B by gravity feed to leg 5B, to lift pot 6B whereupon it is pneumatically transferred to reactor C through lift pipe 7B. The catalyst stream is then circulated through reactor C by gravity feed to leg 5C, lift pot 6C, and lift pipe 7C to reactor D. Catalyst is then withdrawn through gravity feed to leg 5D to lift pot 6D. From lift pot 6D the catalyst is intermittently withdrawn through reforming catalyst return lift pipe 8 to separator 9. Control valves 12A, 12B, 12C, and 12D regulate the flow of catalyst from each of the respective reforming reactors, providing a moving bed type of operation to the reforming system. Generally, the catalyst is regenerated in cycles of from 1/2 to 30 days, depending upon the reformer operating conditions and regenerated facility capacity. Lines 10, 11 A, B, C and D, and 12 A, B, C and D supply a hydrogen lift gas to each of the lift pots 6 and lift pipes 7 and 8, although any other suitable lift gas may also be employed.

The hydrodesulfurization catalyst circulation loop, generally indicated at 13, comprises catalyst feed conduit 4 and control apparatus 32 plus block valve 33, hydrodesulfurization reactor E, gravity transfer pipe 14, lift pot 6E, and pneumatic hydrodesulfurization catalyst return pipe 15. The rate of descent of the catalyst through the hydrodesulfurization reactor E may be controlled by a valve on line 14 or by controlling the lift gas as will be understood by those skilled in the art. Catalyst is withdrawn through valved transfer pipe 14 at a rate such that the catalyst inventory is regenerated in a cyclic fashion. Withdrawn hydrodesulfurization catalyst intermittently flows in lift pot 6E and is transferred through return pipe 15 to the separator 9 so that the catalyst inventory may be regenerated with the desired frequency. A hydrogen lift gas is supplied through lines 10, 11, and 12E to lift pot 6E and return lift pipe 15 to provide the pneumatic force for carrying the granular catalyst to separator 9 for regeneration.

While the particular hydrodesulfurization system shown is a one reactor system, any number of hydrodesulfurization reactors may also be employed. Any conventional hydrodesulfurization catalyst is also suitable for use in the instant invention, including without limiting the instant invention, nickel and molybdenum or salts thereof on an inorganic refractory support; nickel and tungsten or salts thereof on an inorganic refractory support; cobalt and molybdenum or salts thereof on an inorganic refractory support; and nickel-cobalt-molybdenum or salts thereof on an inorganic refractory support. Particularly suitable are those hydrosulfurization catalysts comprising one or more members of the group consisting of cobalt and molybdenum, nickel and molybdenum, nickel and tungsten, their oxides, their sulfides, and mixtures thereof on an alumina support.

During the hydrodesulfurization process, the

naphtha charge or hydrocarbon stream boiling in the gasoline boiling range is fed by means, not shown, into the hydrodesulfurization reactor where, in admixture with a hydrogen stream, it reacts in the presence of the descending hydrodesulfurization catalyst to convert the sulfur-containing impurities to H_2S and other products which are then removed from the process stream by means well known to those skilled in the art. The desulfurized naphtha stream is typically fed into the catalytic reforming apparatus for conversion to a higher octane product. This invention is not limited, however, to situations where the same feed is processed by each species of catalyst served by the common regenerator. Each catalyst species may also process two different feeds. While the particular process conditions for each of these processes are well known to the art, generally, it may be said that the reforming process is accomplished under adiabatic conditions at a pressure of about 50 psia to about 550 psia, reactor inlet temperature between about 850° and 1,000°F, a hydrogen rate of 200 to 10,000 standard cubic feed per barrel (s.c.f.b.) of charging stock, and a liquid hourly space velocity (LHSV) of between 1 to 12 volumes of hydrocarbon per hour per volume of catalyst. The hydrodesulfurization process proceeds at a temperature of about 500°F to 725°F, an LHSV of about 1 to about 10 volumes of hydrocarbon per hour per volume of catalyst, and a hydrogen-to-hydrocarbon ratio of about 300 s.c.f.b. to about 5,000 s.c.f.b.

The process of the instant invention is thus particularly advantageous for use in a combination process wherein a naphtha stream is hydrodesulfurized in a naphtha-hydrodesulfurization zone to reduce the sulfur contained therein to a level not exceeding 5 ppm and preferably less than 1 ppm sulfur by reaction with hydrogen on a catalytic surface. The resulting desulfurized effluent is then reformed in a regenerative reforming process to provide increased yields of high octane gasoline blending components. During these processes, the catalyst particles become encrusted with coke and other deposits, and gradually decline in catalytic activity. When this activity declines to an undesirable level, regeneration of the catalyst is necessary. To effectuate this regeneration, in the present invention, catalyst is alternately withdrawn from each of these systems and regenerated in alternating regeneration cycles. The reactivated catalyst from one cycle is transferred back to its process system and a new regeneration cycle is initiated. By alternately withdrawing, regenerating, and then returning a portion or even all of each process' catalyst inventory, the method and apparatus of the present invention enables a single regeneration facility to maintain the activity of two different catalysts at optimum levels.

In accordance with this scheme, a stream of spent catalyst is alternately withdrawn from the reforming system 1 and the hydrodesulfurization system 13, and transferred via pneumatic return pipe 8 or 15 to separator 9. The separator 9 functions to remove separate residual hydrocarbon, fines, and other debris from the catalyst stream. The stream of catalyst in its regeneration cycle collects in the separator 9 and is purged off the residual hydrocarbon and

other matter through vent 18 by a hydrogen gas stream.

After purging, the catalyst stream in its regeneration cycle is transferred through valved feed pipe 19 to regenerator 20 where the spent catalyst particles are reactivated by contact with regeneration gasses at elevated temperatures. The regenerator 20 may be of any suitable design well known to those skilled in the art, such as that described in U.S. Patent No. 3,647,680. Moreover, the regenerator 20 may be a continuous or cyclically operated facility. A typical continuous regenerator comprises a carbon burn-off zone, and/or halogenation zone, and/or a reduction zone, and/or also a drying zone. All of these functions and others if needed for a particular catalyst species may also be accomplished in a cyclically operated apparatus.

When the regenerator 20 is operated in a continuous manner, typically the catalyst stream flows downwardly and is contacted with an oxidizing gas at controlled temperatures and pressure. The specific contact time, oxygen content, and temperature used for the carbon burn-off depend, of course, upon the particular catalyst undergoing regeneration. A certain oxygen content and temperature which would optimally regenerate one catalyst could actually decrease the activity of another catalyst. Accordingly, different carbon burn-off conditions may be employed for each catalyst. After substantially all the carbonaceous matter accumulated on the catalyst particles has been removed therefrom, the catalyst stream is contacted with an activating gas whose identity depends on the chemical composition of the catalyst. In the instance of a reforming catalyst, this gas may be a hydrogen reducing gas, although mixtures of steam and oxygen are often used for the activation of hydrodesulfurization catalysts such as the molybdenum-cobalt catalysts.

The particular procedure used for the regeneration step may include any suitable procedure well known to the art. Generally, these procedures comprise subjecting a deactivated and carbonized catalyst to oxidation with dilute oxygen to remove the oxidizable carbon therefrom at controlled temperatures and pressure. The oxygen is diluted to a suitable partial pressure by admixture with a suitable inert gas such as nitrogen, flue gas, or even steam. Following carbon removal, the catalyst is reactivated by exposure to a suitable activating gas such as hydrogen or a mixture of steam and oxygen. Reforming catalysts and those hydrodesulfurization catalysts which contain a platinum group metal are generally activated by contact with a hydrogen reducing gas. After activation, the catalyst is optionally sulfided, depending of course upon the chemical composition of the particular catalyst. U.S. Patent No. 4,007,131, herein incorporated by reference, describes one particularly suitable regeneration procedure for the regeneration of a hydroprocessing catalyst in which the catalyst stream is contacted with a stream of inert gas initially containing about 0.1 to 4.0 volume percent oxygen at an initial temperature of about 600°F to 1,200°F, a pressure of at least about 50 PSIG and then increasing the oxygen concentration to about 1.0 to 10.0 volume percent and/or increasing the

temperature to about 800°F to 1,200°F. However any suitable regeneration procedure known to the art may be utilized in the instant invention.

In Figure 2, the circulation loop for conveying the regeneration gasses to the regenerator will be understood by those skilled in the art and is shown as comprising a heater 30, a compressor 25, heat exchanger 26, and cooler 31. Compressor 25 circulates a suitable regeneration gas, such as hydrogen 21, nitrogen 22, air or O₂ 23, or flue gas 36, through inlet line 24 to the regenerator 20. The heater 30 regulates the temperature of the regeneration gasses entering the regeneration vessel. The used regeneration gasses are removed through line 29 to a flare or are circulated through line 27, heat exchanger 26, and cooler 31 for entrance back into the system through line 36, or removal through flare 38. The heat exchanger 26 utilizes the heat of the used regeneration gasses to preheat those entering the regenerator vessel 20. Cooler or waste boiler 31 removes and/or conserves any residual heat of the used gasses before their departure from the system through flare 38. Additionally, cooler 31 reduces the temperature of those gasses which are recirculated through line 36 back into the system. A halogenation or sulfiding gas may optionally be introduced through line 28 to the regenerator vessel 20. To those skilled in the art, it may be desirable to have other equipment or modifications in order to achieve optimum regeneration results, and it is not intended to limit the regeneration system to only the system shown. Any regeneration system known in the art may be advantageously employed in the instant invention.

The operation and method of the instant invention is as follows: with block valves 33 and 16 on hydrodesulfurization catalyst return lines 4 and 15 respectively closed, a stream of spent reforming catalyst is pneumatically transferred through return line 8 from lift pot 6D to separator 9. With the valves on line 19 closed, residual hydrocarbon and debris is purged from the catalyst stream through vent 18 by hydrogen flow from lines 11 and 12 and return line 8. After purging, the catalyst descends through line 19 to regeneration vessel 20 where it is first decarbonized by oxidation with a heated nitrogen-oxygen admixture of flue gas-oxygen admixture while the halogen content is adjusted. The regenerated reforming catalyst is then dried by contact with a hot stream of nitrogen or flue gas and air through lines 23 and 24. Subsequently, the reforming catalyst is reactivated by reduction with a hydrogen gas flowing through lines 28 and 29. With hydrodesulfurization feed leg control valve 33 remaining closed, valves 32 and 34 are opened and the reactivated reforming catalyst is returned to a reactor A. This completes the reforming catalyst regeneration cycle.

Between regeneration cycles it is desirable to purge the regeneration unit to remove any contaminants which may have a deleterious effect on the activity of the incoming catalyst species. Conveniently, the regeneration unit may be purged by introducing an inert gas, optionally containing oxygen, through lines 22, 23 and 24, to sweep any contaminants out of the regeneration unit. Prefer-

ably, this purging step is performed between each regeneration cycle to preclude contamination or poisoning of the incoming catalyst species.

Closing of block valve 17 and 34 on return line 8 and 3, respectively, then switches the system to the hydrodesulfurization catalyst regeneration cycle. Not shown may be a holding apparatus inside or outside reactor A for holding reforming catalyst during the regeneration of hydrodesulfurization catalyst. Hydrodesulfurization catalyst is transferred from lift pot 6E through return line 15 to the separator 9. The hydrodesulfurization catalyst is then purged and conducted to regenerator vessel 20 where it undergoes a regeneration optimal for its chemical composition. Generally, the catalyst will be decarbonized by an oxidizing gas flowing through line 24. It is generally then activated by sulfiding and then reduced with hydrogen. The regenerated catalyst stream descends through feed line 2 and control valve 32, and feed leg 4 and valve 33 into the reactor E. After closing of block valve 16 and 33, the system is then alternated for the regeneration of reforming catalyst. A holding apparatus may also be employed outside or inside of reactor E for holding the hydrodesulfurization catalyst during the regeneration of the reforming catalyst.

The method of the instant invention thus contemplates alternately regenerating a stream of a first catalyst, and then a stream of a second catalyst. By properly adjusting the length of each regeneration cycle, a single regeneration facility can maintain the optimum catalyst activity in both processes.

The present invention is, of course, not limited to the particular embodiment above described. It may advantageously be applied to different petroleum treatment processes and to more than two such processes, as would be obvious to those skilled in the art. Nor need it be limited to those processes employing gravitating beds. With minor modifications, the instant invention may be applied to processes utilizing fluidized beds. It may also be advantageously utilized in systems in which two different processes share the same vessel, or where a mechanical mixture of two chemically different catalysts are employed.

Figure 3 illustrates an alternative embodiment of the instant invention, similar to Figure 2, in which a single reforming reactor 50, containing multiple treatment zones 51, 52 and 53 is employed instead of the four-reactor reforming system shown in Figure 2. In this embodiment, fresh or freshly regenerated catalyst is pneumatically lifted by a lift gas through lines 93 and 99 from lift pot 69, feed conduit 71, and valve 73 to the reactor 50. Thereupon, the reforming catalyst flows from one successive reforming reaction zone to the next by gravity flow and does not require therefore pneumatic conveyance systems. Spent reforming catalyst collects in collection vessel 55 and is intermittently transported via lift pot 57, return line 59, and valve 61 to the regenerator 63 by lift gas through line 93. After regeneration, the reforming catalyst descends through line 65 and valve 67 by gravity to lift pot 69 for return to the reforming reactor 50. The regeneration unit is then purged of any possible contaminants by an inert

sweep gas.

In the hydrodesulfurization catalyst regeneration cycle, spent catalyst descends from reactor 85 via line 86 to lift pot 87 where it is lifted by lift gas through lines 93 and 95 to the regenerator 63. After regeneration, the reactivated catalyst descends by gravity through line 75 and valve 77 to lift pot 79. Lift gas through lines 93 and 97 then conveys the regenerated catalyst back to the hydrodesulfurization reactor 85 via feed line 81 and valve 83.

Figure 4 illustrates the application of the instant invention to a treatment process, generally indicated at 1', wherein a mechanical mixture of two chemically distinct catalyst or components are employed.

A fresh mixture of the catalytic components descends from feed vessel 22' through feed conduit 2' and control valve 23' into reactor A'. There, the mixture is contacted with a hydrocarbon charge in a hydroconversion process. As the catalyst descends through reactor A', its catalytic activity is gradually reduced due to the accumulation of coke and/or other deposits thereon. The rate of descent of the catalytic mixture through reactor A' is controlled by a valve on gravity feed leg 3' or the lift gas through line 6' and 7'. The rate of movement through valved leg 3' is adjusted so that the entire catalyst inventory is replenished with a frequency sufficient to provide desirable levels of catalytic activity. Spent catalyst is intermittently transferred through pneumatic return line 5' to the separator 8'. A hydrogen gas stream flowing through lines 6' and 7' provides a propellant force to the particles of the catalytic mixture. Lines 6' and 7' also provide a source of hydrogen for purging the spent stream of residual hydrocarbon in separator 8'. A separate purge stream may also be provided in separator 8'.

In the separator 8', the spent stream is first purged of residual hydrocarbon and other debris through vent 9'. After purging, the separator apparatus may be used to separate the spent mixture into larger and smaller particle size streams by means well known in the art. The larger size component collects in the bottom section of separator 8', and is withdrawn through line 11' to holding vessel 13'. The smaller size component is collected in a top section of the separator 8', and is conveyed out of the separator through line 10' to holding vessel 12'. A stream of each component is then alternately withdrawn through either line 14' and control valve 15' or line 16' and control valve 17' into regenerator feed conduit 18'. Control valve 19' on conduit 18' controls the rate of descent into regenerator 20'. In the regenerator 20', each component is regenerated by a process tailored to its chemical composition.

The circulation loop for the regeneration gasses is shown as being identical with that of Figure 1, comprising a compressor 28' for circulating hydrogen 24', nitrogen 25', air or O₂ 26', or flue gas 36' through feed line 27', heat exchanger 29', and heater 30' to the regenerator 20'. The depleted regeneration gasses are either transported to flares 35' or 31' via line 32', or are directed back into the system through line 36'. A waste heat boiler or cooler 30' is provided to cool the used gas for reuse and to conserve any residual heat. Additional treating gas or gasses such

as a halogen or sulfiding gas may optionally be contacted with the component stream through line 33' and vented via line 31'. The particular mixture desired to be regenerated may, of course, require other equipment or modifications to this circulation loop, obvious to one skilled in the art, to obtain optimum regeneration.

After reactivation, the regenerated component descends through line 21' to the catalyst hold vessel 22'. The catalyst hold vessel 22' temporarily stores the reactivated component while the regenerator is first purged by an inert gas and then while a spent stream of the other catalytic component is being regenerated. Upon reactivation of the second component, it is fed through line 21' to catalyst hold vessel 22' where it is mechanically mixed by means known to the art with the stream of the first component. The combined reactivated stream is then fed back into the reactor A' for hydrotreating. Thereafter, another deactivated stream of catalyst mixture is transferred through return line 5' whereupon it is then separated into its components which are alternately regenerated, mixed, and then returned to the process reactor.

It should be obvious to one skilled in the art that the system described in Figure 4 is not limited to a catalyst mixture containing only two components, but with minor modification, can also be applied for commonly regenerating a catalyst mixture having any number of components. It should be equally obvious that the instant invention may also be applied with minor modifications to a system wherein two different hydrotreating processes occur in the same vessel, such as those with a staged structure. In that situation, each separate stage is provided with its own feed leg 3' and lift pot 4' communicating with the return pipe 5', by which used catalyst is alternately withdrawn from each stage for regeneration.

CLAIMS

1. A method for operating a catalyst regeneration apparatus to enable at least two catalytically active species employed in at least one chemical reaction process to utilize a common regeneration apparatus, said method comprising operating said regeneration apparatus in alternating regeneration cycles, each of said catalytically active species having a specific regeneration cycle associated therewith, and each of said cycles comprising the steps of:

- a) transporting a stream of said catalytic species which has suffered a decrease in activity by exposure to chemical reaction conditions to said regeneration apparatus;
- b) treating the catalytic species therein to adjust its activity to desirable levels; and
- c) returning the treated catalytic species to its respective chemical reaction process.

2. A method according to Claim 1, further comprising purging said regeneration unit between each regeneration cycle.

3. A method according to Claim 1 or 2, wherein said catalytic species have different chemical compositions.

4. A method according to Claim 1, 2 or 3, wherein said catalytic species are physically different.

5. A method according to any one of the preceding claims, wherein said catalytic species differ in degree of deactivation.

6. A method according to any one of the preceding claims, wherein said stream of catalytic species is transported pneumatically.

7. A method according to any one of Claims 1 to 5, wherein said stream of catalytic species is transported mechanically.

8. A method according to any one of the preceding claims, wherein said treatment step is a continuous process.

9. A method according to any one of the preceding claims, wherein said treatment step is a cyclic process.

10. A method according to any one of the preceding claims, wherein said catalytic species is treated by removing a deactivating material to increase its activity.

11. A method according to Claim 10, wherein said deactivating material is a carbonaceous deposit.

12. A method according to Claim 11, wherein the carbonaceous material is removed by exposing said catalytic species to an inert oxygen-containing gas under conditions of controlled temperature and pressure.

13. A method according to any one of the preceding claims, wherein said catalytic species is treated by exposure to an activating agent.

14. A method according to Claim 13, wherein the activating agent is selected from a hydrogen containing gas, a hydrogen rich gas, a halogen containing gas, a sulfur containing gas, a water containing gas, and mixture thereof.

15. A method according to any one of the preceding claims, wherein said catalytic species are treated by contact with a drying agent.

16. A method according to Claim 15, wherein the drying agent is a solid drying agent.

17. A method according to Claim 15, wherein the drying agent is an inert gas at elevated temperatures.

18. A method according to any one of the preceding claims, wherein said catalytic species are regenerated by exposure to an oxygen-containing gas, an activating agent, and a drying agent under conditions of controlled temperature and pressure.

19. A method according to any one of the preceding claims, wherein said catalytic species are species employed in the same chemical treatment process.

20. A method according to Claim 19, wherein the catalytic species are species employed in processing different feedstocks in the same chemical treatment process.

21. A method according to Claim 19, wherein the catalytic species are species employed in treating the same feedstock in two or more successive steps of chemical treatment.

22. A method according to Claim 19, 20 or 21, wherein the catalytic species are species employed in an organic chemical treatment process.

23. A method according to Claim 22, wherein the chemical treatment process is catalytic hydrocrack-

ing, isomerization, hydrogenation, alkylation, dehydrogenation, polymerization, oligomerization, reforming, or hydrodesulfurization.

24. A method according to any one of Claims 1 to 18, wherein the catalytic species are species in different chemical treatment processes.

25. A method according to Claim 24, wherein said catalytic species are employed in different chemical treatment processes on the same feeds-tock.

26. A method according to Claim 24, wherein the catalytic species are species employed in different chemical treatment processes on different feeds-tocks.

27. A method according to Claim 24, 25 or 26, wherein said chemical treatment processes are organic chemical treatment processes.

28. A method according to Claim 27, wherein the organic chemical treatment processes are combinations of the processes selected from catalytic hydrocracking, isomerization, hydrogenation, alkylation, dehydrogenation, polymerization, oligomerization, reforming, and hydrodesulfurization.

29. A method according to Claim 28, wherein one of the catalytic species is a reforming catalyst, and another of the said species is a hydrodesulfurization catalyst.

30. A method according to Claim 29, wherein the hydrodesulfurization catalyst is selected from nickel and molybdenum and salts thereof on an inorganic refractory support; nickel and tungsten and salts thereof on an inorganic refractory support; cobalt and molybdenum or salts thereof on an inorganic refractory support; nickel-cobalt-molybdenum and salts thereof on an inorganic refractory support; and combinations thereof.

31. A method according to Claims 29 or 30, wherein the reforming catalyst is selected from platinum-halogen on an inorganic refractory support, platinum-halogen-germanium or an inorganic refractory support, platinum-halogen-iridium on an inorganic refractory support, platinum-halogen-rhenium on an inorganic refractory support, and combinations thereof.

32. A method according to Claim 1 substantially as hereinbefore described with reference to, and as illustrated in the accompanying drawings.

33. Apparatus for the regeneration of at least two catalytically active species, employed in at least one chemical treatment process, requiring different regeneration procedures, comprising:

- a) a regeneration unit;
- b) means for supplying a regeneration agent to said regeneration unit;
- c) means for alternately supplying a stream of each of said catalytic species to said regeneration unit for treatment therein; and
- d) means for alternately discharging a stream of each of said catalytic species, after treatment, from said regeneration unit.

34. An apparatus according to Claim 33, further comprising at least one chemical process reactor employing said catalytic species therein and having attached thereto said supplying means and said discharging means for transporting said catalytic

species between said reactor and said regeneration unit.

35. An apparatus according to Claim 33, or 34, wherein said supplying means comprises a selectively operable pneumatic transfer apparatus.

36. An apparatus according to Claim 35, wherein said pneumatic transfer apparatus comprises a pneumatic lift pot and transport conduit.

37. An apparatus according to Claim 33 or 34, wherein the supplying means comprises a mechanical transfer apparatus.

38. An apparatus according to Claim 33, wherein said means for supplying said regeneration agent to said regeneration unit comprises:

- a) a compressor to circulate said agent;
- b) a heat exchanger for transferring the heat from an effluent stream of regeneration agent to an influent stream of regeneration agent for heat conservation;
- c) at least one heater to control the temperature of the regeneration agent entering the regenerator unit; and
- d) a cooler for reclaiming residual heat from an effluent stream of regeneration gas before it is vented to the atmosphere.

39. An apparatus according to any one of Claims 33 to 38, further comprising a dryer for removing water from the regeneration agent before introduction into the regeneration unit.

40. An apparatus according to any one of Claims 33 to 39, further comprising means for removing undesirable gaseous components of said regeneration agent.

41. An apparatus according to any one of Claims 33 to 40, further comprising at least one separator connected to said supplying means upstream of said regeneration unit.

42. An apparatus according to any one of Claims 33 to 41, wherein said process reactor is a hydrodesulfurization reactor, a reforming reactor, an hydrocracking reactor, an isomerization reactor, an hydrogenation reactor, an alkylation reactor, a dehydrogenation reactor, a polymerization reactor, an oligomerization reactor, or a combination thereof.

43. An apparatus according to Claim 42, wherein at least one hydrodesulfurization reactor and at least one reforming reactor is employed.

44. An apparatus according to any one of Claims 33 to 43, wherein a single process reactor is employed which is alternately used for at least two different functions.

45. An apparatus according to any one of Claims 33 to 44, wherein said discharging means for alternately returning catalytic species to each of said reactors from said regeneration unit further comprises a separate holding vessel for each of said catalytic species connected to each of said reactors upstream thereof.

46. An apparatus according to any one of Claims 33 to 45, wherein said means for discharging said catalytic species from said regeneration unit comprises a mixing vessel and a return conduit.

47. An apparatus according to any one of Claims 33 to 46, wherein said discharging means comprises a pair of selectively operable return conduits.

48. An apparatus according to any one of Claims 33 to 47, wherein said regeneration unit includes a carbon burn-off zone.
49. An apparatus according to any one of Claims 33 to 48, wherein said regeneration unit includes a halogenation zone.
50. An apparatus according to any one of Claims 33 to 49, wherein said regeneration unit includes a sulfiding zone.
51. An apparatus according to any one of Claims 33 to 50, wherein said regeneration unit includes a drying zone.
52. An apparatus according to Claim 33 substantially as hereinbefore described with reference to, and as illustrated in Figures 2 to 4 of the accompanying drawings.

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